

ABSORPTION SPECTRA OF THIN FILMS COMPOUNDS IN THE RbCl-CuCl SYSTEM

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Compounds of the RbCl-CuCl system have been studied by many authors. Basically, the search was conducted for the composition of the compound with the maximum ionic conductivity. Different compositions of the superionic compound were proposed - RbCu₃Cl₄ and Rb₂Cu₃Cl₅ [1], Rb₃Cu₇Cl₁₀ [2], Rb₄Cu₉Cl₁₃ [3]. However, according to the phase diagram, compounds RbCu₂Cl₃, Rb₂Cu₃Cl₅ and Rb₂CuCl₃ are formed in the RbCl - CuCl system [4]. RbCu₂Cl₃ compound has a high ionic conductivity $5 \cdot 10^{-3} \Omega^{-1}\text{cm}^{-1}$ at room temperature. The absorption spectra of compounds of the RbCl-CuCl system have not been studied, although the crystal structure of many of the above compounds has been studied in detail.

The (RbCl)_{1-x}(CuCl)_x thin films were prepared by evaporating in a vacuum a melt of a mixture of pure RbCl and CuCl powders of a given molar composition on quartz substrates heated to 100°C, followed by annealing the films for an hour at the same temperature. The study of the absorption spectra of thin films (RbCl)_{1-x}(CuCl)_x showed that in the concentration range $0.5 \leq x \leq 0.66$ only two compounds with a stable spectrum are formed – RbCu₂Cl₃ and Rb₂Cu₃Cl₅ (Fig. 1). We failed to synthesize the compound Rb₂CuCl₃.

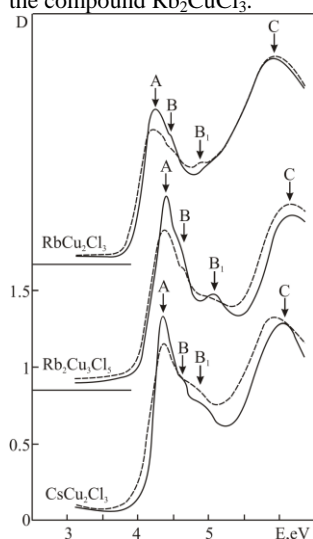


Fig. 1. Absorption spectra of RbCu₂Cl₃, Rb₂Cu₃Cl₅ and CsCu₂Cl₃ thin films at T = 90K (1) and 290K (2).

In the absorption spectra of thin films of RbCu₂Cl₃ and Rb₂Cu₃Cl₅ (Fig. 1), two narrow intense bands A and B, a weak band B₁ and a wide short-wavelength band C are observed. With increasing temperature, bands A and B shift to the long-wavelength region of the spectrum, broaden and weaken due to the exciton-phonon interaction (EPI), which indicates their exciton origin. The band C is not very sensitive to temperature and corresponds to interband transitions. The spectral positions of the absorption bands, the band gap E_g , the binding energy R_{ex} , and the exciton radius a_{ex} in RbCu₂Cl₃ and Rb₂Cu₃Cl₅ are given in Table 1.

In terms of the structure of the spectrum and the position of the main absorption bands, the spectra of thin films of RbCu₂Cl₃ and Rb₂Cu₃Cl₅ are close to the spectrum of the previously studied compound CsCu₂Cl₃ [5] (Fig. 1, Table 1). In CsCu₂Cl₃, excitons have a cationic character, are localized in the structural elements of the crystal lattice CuCl₄³⁻ and their spectrum is interpreted proceeding from the state of the Cu⁺ ion in a tetrahedral environment with Cl⁻ ions [5].

Table 1. Spectral position of absorption bands, bandgap width E_g , binding energy R_{ex} and exciton radius a_{ex} in compounds.

Compound	E_{mA} , eV	E_{mB} , eV	E_{mB1} , eV	E_{mC} , eV	R_{ex} , eV	E_g , eV	a_{ex} , Å
RbCu ₂ Cl ₃	4.21	4.475	4.92	5.9	0.185	4.4	12.8
Rb ₂ Cu ₃ Cl ₅	4.36	4.63	5.08	6.2	0.21	4.57	11.5
CsCu ₂ Cl ₃	4.33	4.615	4.92	6.05			

The absorption spectra of compounds are linked to their crystal structure. Common to the crystal structures of the compounds RbCu₂Cl₃, Rb₂Cu₃Cl₅, and CsCu₂Cl₃ is the presence of structural elements CuCl₄³⁻ in them [6, 7, 8]. Apparently, the absorption spectra of thin films of RbCu₂Cl₃ and Rb₂Cu₃Cl₅, like the spectrum of CsCu₂Cl₃, are due to transitions in the Cu⁺ ion. Low-frequency excitations of the free Cu⁺ ion correspond to the transition $^1S_0 \rightarrow ^1D_2$. For the Cu⁺ ion located in the center of the tetrahedron, 1S_0 transforms into 1A_1 and the 5-fold degenerate state 1D_2 splits into levels 1T_2 and 1E . According to the selection rules for the local group T_d [5], the optical transition to a lower level 1T_2 is allowed, but the transition $^1A_1 \rightarrow ^1E$ is prohibited. Since the Cu⁺ ion is somewhat displaced from the center of the tetrahedron in the lattices of the studied compounds, the local group decreases to C_{2v} . Under the action of a weak axial intracrystalline field the prohibition on the transition $^1A_1 \rightarrow ^1E$ is partially lifted, and the level 1T_2 is split into components. Correspondingly, the intense exciton bands A and B in the studied compounds, such as in CsCu₂Cl₃, correspond to the transition $^1A_1 \rightarrow ^1T_2$, and the weak band B₁, to the transition $^1A_1 \rightarrow ^1E$.

From the above, it follows that excitons in RbCu₂Cl₃ and Rb₂Cu₃Cl₅ are localized in the structural elements CuCl₄³⁻ of the crystal lattice. With this localization, the top of the valence band in the studied compounds, such as in CuCl, is formed by the 3d states of the Cu⁺ ion and the 3p states of the Cl⁻ ion, and the conduction band is formed by the 4s states of the Cu⁺ ion.

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